Coordination Frameworks Containing the Pyrimidin-4-olate Ligand. Synthesis, Thermal, Magnetic, and \textit{ab Initio} XRPD Structural Characterization of Nickel and Zinc Derivatives

Elisa Barea,† Jorge A. R. Navarro,*† Juan M. Salas,*† Norberto Masciocchi,*‡ Simona Galli,‡ and Angelo Sironi§

Departamento de Química Inorgánica, Universidad de Granada, Av. Fuentenueva S/N, E-18071 Granada, Spain, Dipartimento di Scienze Chimiche, Fisiche e Matematiche, Università degli Studi dell’Insubria, via Valleggio 11, I-22100 Como, Italy, Dipartimento di Chimica Strutturale e Stereoquimica Inorganica, Università degli Studi di Milano, via Venezian 21, I-20133 Milano, Italy, and Istituto di Scienze e Tecnologie Molecolari del CNR e Istituto Nazionale di Fisica della Materia, via Golgi 19, I-20133 Milano, Italy

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Extended coordination frameworks containing the pyrimidin-4-olate ligand (4-pymo) and Zn(II) and Ni(II) metal ions have been obtained by solid state reactions and have been fully characterized by spectroscopic, thermal, and magnetic measurements and by \textit{ab initio} XRPD. The reaction of ZnO and 4-Hpymo at 140 °C gives a solid microcrystalline phase, Zn(4-pymo)$_2$ (1). Its 3D framework contains Zn(II) centers linked by 4-pymo ligands acting in two different coordination modes, namely, the N,N’- and the N,O-exo-bidentate ones, which result in a pseudotetrahedral ZnN$_2$O chromophore. Thermal treatment of the “molecular” Ni(4-pymo)$_2$(H$_2$O)$_4$ complex (2) above 140 °C gives an anhydrous amorphous material analyzing as Ni(4-pymo)$_2$ (3a). Further heating of this material above 388 °C results in the formation of the microcrystalline layered Ni(4-pymo)$_2$ species (3b), in which Ni(II) centers are bridged by N,O-exo-bidentate 4-pymo ligands (assisted by longer Ni…N contacts). The thermal dependence of the magnetic susceptibility has been studied for the paramagnetic species 2 and 3a. 2 shows a weak antiferromagnetic interaction [$J = -0.313(5)$ cm$^{-1}$] transmitted through the multiple H-bonding interactions between the exocyclic pyrimidine and water oxygen atoms coordinated to the metal centers. 3a behaves as a 2D Heisenberg antiferromagnet with $J = -4.11(3)$ cm$^{-1}$.

Introduction

The synthesis of solid materials frequently requires high temperature and/or high pressure solid state reactions. This strategy may involve either a single precursor, implying transformation of one phase to another, or reaction of two or more components to give a single product. Although very common in the field of solids of high technological interest, \textit{e.g.} superconductors, semiconductors, and magnetic materials,\textsuperscript{1} this synthetic methodology is rarely applied in the preparation of extended coordination compounds.\textsuperscript{2,3} A typical consequence of solid state reactions is that microcrystalline powders (not single crystals!) are obtained. Therefore, most researchers employ either crystallization from solution\textsuperscript{4} or hydrothermal methods\textsuperscript{5} in order to obtain single crystals suitable for conventional structural analysis. However, when

\textsuperscript{1} Elliot, S. \textit{The Physics and Chemistry of Solids}; John Wiley & Sons: Chichester, 2000.

single crystals lack, microcrystalline powders can be conveniently characterized using ab initio X-ray powder diffraction (XRPD) which, in the recent past, has been shown to afford limited, but otherwise inaccessible, structural information.6

We are currently interested in the coordination chemistry of 2-hydroxypyrimidine (2-Hpymo) and 4-hydroxypyrimidine (4-Hpymo), see Chart 1, which are ideally suited for the construction of extended coordination frameworks with rich structural,7 thermal,8 magnetic,2a and sorptive2c,9 properties. In the present contribution, we describe Ni, 2D-, and Zn, 3D-polymers, based on the versatile 4-pymo ligand, and show the suitability of XRPD for their structural characterization.

Experimental Section

General Methods. 4-Hydroxypyrimidine (4-Hpymo, from Aldrich Chemical Co.) and the other chemical reagents and solvents were acquired from available commercial sources and used as received. IR absorption bands were measured by a Midac FT-IR on KBr pellets. Electronic spectra of solid samples were carried out on a Varian Cary UV–vis–NIR spectrophotometer, and thermogravimetric and differential scanning calorimetric analyses were performed, under dinitrogen, on Shimadzu-TGA-50H/DSC equipment, at heating rates of 10 °C min−1 and 5 °C min−1, respectively (Scientific Instrumentation Center of the University of Granada). Magnetic susceptibility measurements were performed on polycrystalline samples with a Quantum Design MPMS-2SQUID magnetometer (Complutense University) operating in the temperature range 2−300 K and at a magnetic field strength of 10 kG.

Preparation of Zn(4-pymo)2.1, ZnO (1.5 mmol) and an excess of 4-Hpymo (6 mmol) were ground in an agate mortar and heated at 140 °C for 2 h under N2 atmosphere. To eliminate the unreacted 4-Hpymo, the crude product was suspended in acetone (40 mL) and stirred at room temperature for 2 h. The resulting cream-white microcrystalline material was washed with acetone and dried in air. Yield: 95%. Anal. Calcd for C8H6N4O2Zn: C, 38.1; H, 2.5; N, 22.1. IR (selected bands in cm−1): 1641 s, 1483 s, 1425 s, 1366 m, 1311 m, 1020 m, 839 m. UV–vis (nm): 220 vs, 268 vs, 395 s, 652 s, 1140 s, br. Further heating of 30 mg of 3a under dinitrogen at a heating rate of 10 °C min−1 up to 385 °C and then keeping it at this temperature during 5 min afforded a green microcrystalline material (3b). Anal. Calcd for C8H6N2O2Ni(NO3)1.5: C, 36.43; H, 2.29; N, 21.24. Found: C, 36.3; H, 2.4; N, 21.1. IR (selected bands in cm−1): 1609 vs, 1539 s, 1485 s, 1421 s, 1365 m, 1327 s, 1015 m, 841 m. UV–vis (nm): 210 vs, 270 vs, 390 s, sh, 650, 1120 s, br.

X-ray Powder Diffraction Analysis of Zn(4-pymo)2, 1, Ni(4-pymo)(H2O)4, 2, and Ni(4-pymo)2.3b. The powders were gently ground in an agate mortar and then cautiously deposited in the hollow of an aluminum holder equipped with a zero background plate (supplied by The Gem Dugout, State College, PA). Diffraction data (Cu Ka, λ = 1.5418 Å) were collected on a θ/θ Bruker AXS D8 diffractometer equipped with primary and secondary Soller slits (2.3°), divergence, anticrater, and receiving slits (0.5°, 0.5°, and 0.2 mm, respectively), secondary beam curved graphite monochromator, Na(Tl) scintillation detector, and pulse height amplifier discrimination. The generator was operated at 40 kV and 40 mA. Nominal resolution for the present setup is 0.07° 2θ (fwhm of the α1 component) as measured from the Si(111) peak at 28.44°(2θ). Long step-scans with Δ2θ = 0.02° were performed in the ranges 5 < 2θ < 105° with i = 30 s.

For 1 and 3b, indexing was obtained with TREOR9010 [1, monoclinic, a = 11.43, b = 10.52, c = 7.17 Å, β = 122.1°, M(18)11 = 29, F(18)12 = 52(0.010, 35); 3b, tetragonal, a = 6.51, c = 20.93 Å, M(11) = 39, F(11) = 29(0.007, 55)]. The reduced cell of 1 was transformed into the correct trigonal one using the LEPADE program.13 Systematic absences permitted for, among others, K3c and H4/lanld as suitable space groups for 1 and 3b, respectively, later confirmed by successful structure solutions and refinements. Noteworthy, the very slight splitting of the tetragonal [0 0 2] peak into the orthorhombic [2 0 0] and [0 2 0] ones, observed in its cobalt analogue,24 could not be evidenced in the XRPD trace of 3b, which was definitely considered tetragonal. As regards 2, visual inspection of its XRPD trace suggested its strict isomorphous character with the previously reported Co(4-pymo)(H2O)4,24 eventually supported by successful structure refinement. For 1 and 3b, whole profile
Results

Synthesis and Spectroscopy. Reaction at 140 °C in an open vessel of powdered ZnO and an excess of 4-hydroxypteridine (4-Hpymo) gives rise to the formation of a cream-white slurry that, after removal of unreacted 4-Hpymo, yields a cream-white microcrystalline Zn(4-pymo)2 phase (1). It should be noted that the reaction conditions are well below the melting point of 4-hydroxypteridine (164.5 °C), which makes this process a clear example of a two component solid to solid reaction. The resulting material is, however, only thermally stable up to 285 °C (see Figure 2), which is surprisingly low, especially considering the high thermal stability of the related Zn(2-pymo)2 (Tdec = 570 °C).2b

Reaction of 4-hydroxypteridine and nickel(II) salts in aqueous media gives the pale blue-green and poorly soluble microcrystalline Ni(4-pymo)2(H2O)4 material (2). The water content of 2 has been confirmed by thermogravimetric and differential scanning calorimetric analyses (see Figure 2), showing that the four water molecules are lost in a single-step endothermic process at about 150 °C (ΔH = −205 kJ mol−1) giving rise to the anhydrous green amorphous Ni(4-pymo)2 material (3a). Further heating of this sample promotes recrystallization (onset at 388 °C, ΔH = 9.9 kJ mol−1) into the microcrystalline Ni(4-pymo)2 phase (3b). The latter process overlaps with the onset of a further decomposition event, yielding NiO as the final product, which makes it impossible to obtain 3b as a 100% pure sample.18 The presence of the NiO impurity on the crystalline sample is, however, not shown by the XRPD studies, which may be due to the presence of a highly dispersed oxide material. The thermal stability of these systems is significantly lower than that of the previously reported Co(4-pymo)2 (Tdec = 470 °C)2a and related M(2-pymo)2 complexes, which are stable above 500 °C.2b

IR spectra of the samples are indicative of the structural features of these systems (vide infra). Thus, the ν(CO) vibration modes of 1 agree with the simultaneous occurrence of two types of coordination for the 4-pymo ligand, manifested by the strong 1655 and 1607 cm−1 absorption bands. The former absorption can be attributed to the uncoordinated nature of the exocyclic oxygen atom of one of the 4-pymo ligands (showing N,N′-coordination), while the lower frequency peak clearly implies O1 coordination, with the simultaneous weakening of the pertinent C=O1 bond. IR spectra also substantiate the changes taking place on passing from 2 to 3a. The relative small shift of the ν(CO) vibration mode, from 1607 to 1611 cm−1 after O1 involvement in metal coordination, can be attributed to the presence of strong H-bonding interactions in 2 (see below). The 3a to 3b transformation is not accompanied by any shift of the IR absorption bands; indeed, only their sharpening is observed. This fact prompts for their closely related nature.

Table 1. Summary of Crystal Data and Data Analysis Parameters for 1, 2, and 3b

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<td>c, Å</td>
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(15) Bruker AXS 2000: Topas V2.0: General profile and structure analysis software for powder diffraction data.
(18) Thermal and elemental analyses suggest the presence of ca. 6% NiO on the sample.
The electronic spectra of 2, 3a and 3b systems are typical of Ni(II) species in similar octahedral environments. Significant differences are, however, present between the spectra of 2 and 3a. A shift of the d–d absorption bands (reflected by an appreciable color change from pale blue to green) is observed along with a concomitant rise in their intensity. These changes are reflected in the Δo values calculated using the Dou method, which gives values of 9525 and 8930 cm⁻¹ for 2 and 3a, respectively. The


differences in both the Δv values and the intensity of the electronic spectra bands can be attributed to a change of the coordination environment from a trans-D4h (forbidden transitions) to a cis-C2v (allowed transitions) pseudo-octahedral geometry. Additionally, the electronic spectra of 3b show a broadening of the charge transfer bands (with respect to 3a), which may be attributed to the presence of impurities (see above).

Crystal Chemistry. Structure of Zn(4-pymo)2, 1. Among the structures here reported, 1 is the most surprising one. Indeed, it was found to contain, in the highly symmetric R3c space group, surrounded by two crystallographically independent 4-pymo ligands: one bridges metal ions (about 5.72 Å apart) in the common N,N'-exo-bidentate mode, as found, for example, in Zn(2-pymo)2, while the other shows N,O-exo-bidentate coordination (Zn···Zn ca. 7.05 Å). Thus, each zinc ion lies in a nearly tetrahedral N3O environment [Zn−N = 1.958(7), 2.036 (8), and 2.046(7) Å; Zn−O = 2.023(13) Å; N−Zn−N = 106.0(4), 110.2(4), and 121.0(2)°; N−Zn−O = 94.5(4), 107.5(6), and 114.3(5)°] of four different ligands (see Figure 3e).

Interestingly, the N,N'-bound 4-pymo ligands generate, with the zinc ions, parallel rods of [Zn₂(4-pymo)₆]⁺⁺ formulation, elongated along c, which are interconnected in a 3D network by N,O-bridges nearly in plane with ab. At a supramolecular level, the complex structure of 1 can be idealized, neglecting the nature and the orientation of the 4-pymo ligands, as an unprecedented 6₂6₂8₂6₂ network (C₁₀ = 426), built upon polyc connected tetrahedral nodes. Figure 4a shows a portion of the crystal structure, while Figure 4b contains a sketch of the network. Thus, the isomeric forms of Zn(X-pymo)₂ (X = 2 or 4) show rather distinct framework geometries, single diamondoid for X = 2, and an unprecedented uninodal network for X = 4. At variance, the highly porous Cu(X-pymo)₂ species (X = 2, 4), capable of reversible sorption of a number of gases or ions (without changing their framework structure), crystallize, in the cubic Pn3m space group, as strictly isomorphous materials.

Structure of Ni(4-pymo)₃(H₂O)₂, 2. This species is strictly isomorphous with the cobalt analogue and, as already discussed in ref 2a for the latter, contains mononuclear ions of pseudooctahedral geometry, bearing four water molecules and two, mutually trans, 4-pymo ligands bound through their N₁ atoms. The swinging ends of the organic ligands are involved in an extended network of hydrogen bonds (through the N₃ and exocyclic oxygen atoms); accordingly, these “three-dimensional H-bonded polymers” are rather insoluble species. A sketch of the monomer in 2 is shown in Figure 5, together with some pertinent geometrical parameters.

Structure of Crystalline Ni(4-pymo)₂, 3b. This species contains two-dimensional infinite layers of square meshes, where the nickel(II) ions (separated by 6.51 Å, i.e. a or b) are the nodes and the 4-pymo ligands, bridging in the N,O-exoexo-bidentate mode, the rungs. Refined Ni−N₁ and Ni−O₁ bond distances have values of 1.97(1) and 2.08(2) Å, respectively. The (N,O-bridged) M···M distance in 3b, significantly shorter than in 1, can be explained by the presence of an ancillary Ni···N₃ contact [2.29(1) Å], making each Ni(II) ion hexa-, not just tetra-coordinated. Crystal packing of 3b is shown in Figure 6, where the long Ni···N₃ are dashed.

As already discussed for the related Co(4-pymo)₂, 2a 3b shows an extended disorder in the orientation of the 4-pymo ligands; namely: (i) within each layer, all (4-pymo) ligands are rigorously ordered, with a polar head-to-tail sequence of the N,O-bridges, within each rung (running along a or b), for obvious stereochemical reasons; (ii) each rung is, however, independent and may, or may not, adopt the same polarity of the adjacent ones; in addition, (iii) loss of coherence in the 4-pymo orientation is also caused by the disordered stacking of the layers along c. Thus, the highly symmetric I4/amd space group results from this multiple disordering effect; for the reader, an ordered structure is drawn by dramatically lowering the crystal symmetry, for example down to P1 (with the aid of a second, crystallographically independent 4-pymo ligand obtained by the 0.25 − y, 0.25 + x, 1.75 − z transformation, Figure 6). Note that this choice, which clearly implies a periodic, but arbitrary, sequence of layers along c, is by no means unique.

Moreover, it is worthy of note that the still uninterpreted orthorhombic, nearly tetragonal, lattice observed in Co(4-
pymo)$_2$ is not observed for 3b, which, thus, behaves regularly, with $a$ and $b$ rungs of equal periodicity.

**Magnetic Characterization.** The thermal behavior of $\chi_M$ (molar susceptibility per nickel atom) and $\mu_{\text{eff}}$ (effective moment per nickel atom) for compounds 2 and 3a is shown in Figure 7. The $\chi_M$ values steadily increase upon cooling; however, in the case of compound 2, they are much higher than in 3a. The different behavior can be more clearly appreciated from the $\mu_{\text{eff}}$ values, which are almost constant for 2 above 60 K. At this temperature, $\mu_{\text{eff}}$ starts to decrease, which is indicative of an antiferromagnetic intermolecular interaction taking place between the Ni(4-pymo)$_2$(H$_2$O)$_4$...
monomers. In the case of 3a, $\mu_{\text{eff}}$ steadily decreases upon cooling, which can be related to its polymeric nature, implying a stronger antiferromagnetic exchange taking place between the heavily distorted pseudo-octahedral metal centers.

The magnetic behavior of 2 has been fitted to the Curie—Weiss law,\textsuperscript{(22)} giving a Weiss temperature value of $-2.15$ K. This can be related to weak intermolecular antiferromagnetic interactions transmitted through the strong H-bonding inter-

actions established between coordinated water molecules and N₃ and O₁ atoms of pyrimidin moieties.

In the case of 3a and presuming its closely related nature to the 3b phase,\textsuperscript{(23)} its magnetic behavior can be conveniently described by eq 1, which is adequate for the description of the high temperature dependence of the magnetic susceptibility on a 2D Heisenberg quadratic-layer antiferromagnet,\textsuperscript{(24)} where the spin Hamiltonian is defined as

$$H = \sum_{\sigma} J S_i \cdot S_j,$$

where $J$ is the exchange interaction, $S_i$ and $S_j$ are the spins at sites $i$ and $j$, respectively, and $\sigma$ is a spin index. The $C_n$ coefficients have been taken from ref 24. Fitting the data to eq 1 gives a value of $g = 2.143(1)$ and an exchange value $J = -4.11(3)$ cm$^{-1}$, which agrees with a significant antiferromagnetic interaction being transmitted through the pyrimidin-4-olate bridges between adjacent nickel(II) centers. For comparative reasons and taking into account that even 2, by means of the hydrogen bond network, can be considered an extended material, we have also fitted its magnetic data to eq 1. The results show a reasonable good fitting with $g = 2.304(1)$ and $J = -0.313(5)$ cm$^{-1}$, which agrees with a small antiferromagnetic interaction being transmitted through the H-bonding interactions between adjacent nickel(II) centers.

Discussion

Table 2 synoptically collects the main features of the recently characterized M(X-pymo)$_2$ species ($X = 2$ or 4), which are discussed hereafter.

Comparative Analysis of the Thermal and Magnetic Properties. The thermal behavior of 2 is closely similar to that of the isomorphous [Co(4-pymo)$_2$(H$_2$O)$_4$]\textsuperscript{2+} material. Indeed, the dehydration process that leads to the formation of an amorphous phase of type M(4-pymo)$_2$ and the posterior recrystallization to crystalline M(4-pymo)$_2$ materials are very


\textsuperscript{(23)} We avoid including the magnetic behavior of 3b due to the impossibility of obtaining it as a pure material.

similar in both the transition temperature ranges and enthalpy values. There are, however, significant differences in the thermal stability of the resulting microcrystalline M(4-pymo)₂ extended phases. While the Co(4-pymo)₂ crystalline phase is thermally stable well above its recrystallization (see Table 2), Ni(4-pymo)₂ possesses a significantly lower thermal stability, starting its decomposition process along with its recrystallization. Moreover, the latter system shows a decomposition temperature value ca. 200 °C lower than that of its 2-pymo analogue.²

The lower thermal stability of the M(4-pymo)₂ systems compared to their M(2-pymo)₂ analogues is further substantiated by 1, which shows a decomposition temperature value ca. 300 °C lower than that of its Zn(2-pymo)₂ analogue. In the latter case, the lower thermal stability of 1 can be partially related to its lower packing efficiency, illustrated by its higher V/Z value (Table 2). However, additional effects should be taken into account to explain the lower thermal stability for the 4-pymo systems: i.e. the asymmetric nature of the 4-pymo bridges which may facilitate the pyrimidine ring activation by the metal ions during the decomposition process.

The magnetic studies performed on 2 clearly show the presence of intermolecular antiferromagnetic interactions taking place between the Ni(4-pymo)₂(H₂O)₄ monomers, which agrees with its H-bonding supported polynuclear character. This result substantiates the efficiency of X-pymo bridges as transmitters of magnetic information even through noncovalent interactions. In the case of 3a, the higher J exchange parameter value further supports the efficiency of 4-pymo bridges as transmitters of magnetic interactions. Moreover, it should also be noted the higher J value found in this case compared to the one found for the related Co(4-pymo)₂ material (see Table 2). This observation is an additional proof of N₃ involvement in Ni coordination and its concomitant octahedral coordination enviroment found in its electronic spectra and structure. Indeed, the N,N′-bridging mode is responsible for the much higher magnetic couplings, up to ~44 cm⁻¹ and ~36 cm⁻¹ for Cu(4-pymo)₂ and Cu(2-pymo)₂, respectively (Table 2).

Comparative Structural Analysis. From the analysis of the structural features of these systems, it can be easily seen that the presence of the exocyclic oxygen atom and particu-

larly its location have a dramatic influence on the stereochemistry at the metal and on the overall packing types. For copper, the influence of the differently substituted ligands is “structurally” marginal but highly affects the shape, size, and hydrophilicity of the cavities.⁹ For the remaining cations, O₃ becomes an “active” ligand and there is no structural analogy between the 2-pymo and 4-pymo derivatives (markedly different chromophores, pymo bridging modes, and supramolecular features being observed). For example, while cobalt, nickel, and zinc 2-pymo derivatives consist of slightly distorted diamondoid frameworks, (i) Co(4-pymo)₂ and Ni(4-pymo)₂, as discussed above, are based on 2D layers (and (ii) Zn(4-pymo)₂, although 3D in nature, shows a new, rather distinct, framework topology.

According to the V/Z values reported in Table 2, we note that the two differently substituted pymo ligands have little effect on the structure compactness (apart from the Zn derivatives), even if binding in completely different modes and appearing in structures of markedly different dimensionality and density.

Finally, Figure 3 collects the relevant partial structures of M₄(X-pymo)₄ “clusters” highlighting the versatility of pymo ligands in terms of (i) hapticity (η⁵ or η⁶); (ii) bridging modes (N₄N’ vs N,O), and (iii) relative orientation, resulting in a variety of coordination geometries of the metals and “clusters” shape.

Conclusions

The present contribution adds new information on the coordination chemistry of the 4-pymo ligand, which is still in its infancy. In particular, we reported the comparative analysis of the structural, thermal, and magnetic properties of a number of polymeric complexes with the 2- or 4-pymo ligands, highlighting important stereochemical differences. Work can be anticipated in the direction of preparing mixed ligand species, to assess the possible formation of solid solutions or segregation effects, and to move to different transition metal ions, in search for new polymeric architectures and functional materials (porous, sorptive, catalytic, and/or magnetic species).

In addition, the use of powder diffraction from conventional laboratory equipment, which made it possible to
structurally characterize a polycrystalline material, Zn(2-pymo)$_2$, with unexpected, and new, overall connectivity, is here emphasized.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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